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 (72) Inventor DEREK SOUTHERN, JOHN BURGESS and JOHN ROPER



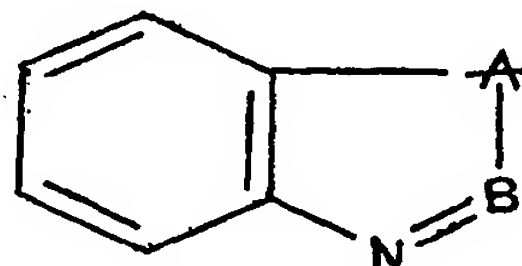
(54) IMPROVED ANTIFREEZE COMPOSITIONS

(71) We, SHELL INTERNATIONALE RE-
 SEARCH MAATSCHAPPIJ N.V., a company
 organised under the laws of The Netherlands,
 of 30 Carel van Bylandtlaan, The Hague, The
 Netherlands, do hereby declare the inven-
 tion, for which we pray that a patent may be
 granted to us, and the method by which it is
 to be performed, to be particularly described
 in and by the following statement:—
 This invention is concerned with antifreeze
 compositions containing corrosion inhibitors.
 Generally, water is used as the heat ex-
 change medium for the cooling system of an
 internal combustion engine for operation at
 temperatures below 0° C. an antifreeze com-
 position should be added. Such antifreeze
 compositions usually contain a water-miscible
 alcohol which can be a lower monohydric
 alcohol, for example methanol or a polyhydric
 alcohol, such as monoethylene glycol, diethyl-
 ene glycol or dipropylene glycol; a polyhydric
 alcohol has the advantage of a high boiling
 point which minimizes vaporisation of the
 alcohol from the cooling system. Under
 normal operating conditions, the metallic
 parts of the cooling system which can contain
 a variety of metals such as copper, solder,
 brass, steel, cast iron and aluminium, are
 susceptible to corrosion; consequently anti-
 freeze compositions usually contain corrosion
 inhibitors. Many corrosion inhibitor systems
 have already been proposed heretofore. How-
 ever, in view of the current trend to favour
 "long life" antifreeze compositions for use
 in sealed cooling systems and also as users
 are nowadays being encouraged to leave anti-
 freeze in conventional unsealed cooling systems
 for longer periods, there is a need for anti-
 freeze compositions capable of meeting more
 stringent end-use requirements than those pre-
 viously available.

The corrosion inhibitor systems used in
 the compositions of the invention have an ex-
 cellent performance to various metals used in
 cooling systems. A particular important ad-

vantage is that this performance is substan-
 tially the same at various diluted concentra-
 tions of antifreeze in water, as will be shown
 hereinafter.

According to the present invention there is
 provided an antifreeze composition, which
 comprises a water-miscible alcohol, an alkali
 metal nitrate, an alkali metal metaborate or
 tetraborate, an alkanolamine phosphate, and
 one or more heterocyclic benzo-compounds
 with the general formula:



in which the benzene ring may contain at
 least one substituent alkyl radical and B
 is a CH, CSH or CSM group (M being an
 alkali metal atom) or a nitrogen atom and
 A represents an oxygen or sulphur atom or
 a NH group, with the proviso that when A
 is an oxygen or sulphur atom, B represents
 a CSH or CSM group only.

The alkanolamine phosphate can be, for
 example, triethanolamine phosphate or triiso-
 propanolamine phosphate, although triethanol-
 amine phosphate is preferred. If desired, the
 alkanolamine phosphate can be prepared *in*
situ by the addition of the calculated quantity
 of an alkanolamine together with phosphoric
 acid, to the water-miscible alcohol. When tri-
 ethanolamine phosphate is used this can be
 formed from commercial grades of triethanol-
 amine containing up to 15% weight of di-
 ethanolamine. The amount of alkanolamine
 phosphate is preferably from 0.1 to 5.0 by
 weight of the antifreeze composition.

It will be understood that an antifreeze
 composition in accordance with the present

invention may be prepared in any convenient manner. The present invention accordingly includes a method of preparing an antifreeze composition, which comprises adding to a water-miscible alcohol in any suitable manner a plurality of components which in combination with said alcohol form an antifreeze composition as hereinbefore defined. Preferably such a composition will contain at least 90 to 95% by weight of a water-miscible alcohol, and if desired, such an antifreeze composition may also contain a minor amount, for example, less than 5% by weight, of water. The preferred water-miscible alcohol is ethylene glycol. Likewise, mixtures of 50 vol. % of ethylene glycol and 50 vol. % of methanol are also very good.

The phosphate component can be added as such or formed *in situ*, preferably by the addition of an alkanolamine and phosphoric acid in a molar ratio such that the pH of a 50% by volume solution of the composition in water, determined by the ASTM Method No. D 1287-58, is between 7.0 and 8.5, for example 7.5 to 8.0.

The preferred alkali metal nitrates are sodium and potassium nitrate. Generally, these salts are used in amounts between 0.1 and 1.0 % by weight of antifreeze composition. An alkali metal nitrate may be present as an optional additional component in amounts between 0.1 and 1.5 % by weight of the antifreeze composition. Sodium and potassium nitrate are preferred. The alkali metal metaborate or tetraborate can also be a potassium or sodium salt, although a sodium salt is preferred on cost grounds; the amount of alkali metal metaborate or tetraborate may be between 0.1 and 4% by weight of the antifreeze composition. Usually a tetraborate, particularly borax, is to be preferred. Mixtures of a tetraborate and a metaborate can be used as well. The amount of heterocyclic benzo-compound can be between 0.05 and 0.5% by weight of the antifreeze composition. Examples of heterocyclic benzo-compounds of the above specified general formula are 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 4-ethyl-2-mercaptobenzothiazole, 2-mercapto-4,5-dimethylbenzothiazole, sodium 2-mercaptobenzothiazole, potassium 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, benzotriazole, 4-methylbenzotriazole, 5-methyl benzothiazole, benzimidazole, 4-methylbenzimidazole, 5-methylbenzimidazole and 5,6-dimethylbenzimidazole; sodium mercaptobenzothiazole or benzotriazole and mixtures thereof are preferred.

If desired, an antifreeze composition in accordance with the present invention can contain 0.0005 to 0.05% by weight or more, by weight, of an antifoam. Examples of suitable antifoams are silicone oils, polyglycols, mineral oils, iso-octanol, C₈ to C₁₂ alcohols, for example, C₇ to C₉Oxo alcohols, organic phos-

phates, alkyl lactates and castor oil soaps. Particularly suitable polyglycols are polyoxypropylene glycols of nominal molecular weight from 950 to 1950 which have been reacted with ethylene oxide to give copolymeric products which contain in their molecular structure up to 30% by weight of ethylene oxide. In general the amount of antifoam should not be greater than 1% by weight of the antifreeze composition. If desired, the antifreeze compositions can contain an organic dye; a minor amount of up to 5% by weight of water can also be present to ensure solubility in the antifreeze composition of the organic components specified. Preferably the pH of a 50vol% solution in water of an antifreeze composition in accordance with the present invention is not greater than 10.0.

The antifreeze compositions of the present invention are particularly suitable for use as for example, 10 to 60% aqueous solutions (on a volume basis), in the cooling systems of internal combustion engines, the particular concentration of the aqueous solution depending on the temperature conditions under which the engines will work. The antifreeze compositions of the present invention can, however, be used as heat exchange media in other machinery or equipment, not necessarily in admixture with water.

The invention is illustrated by means of Examples of which Examples I and III are included for the purpose of comparison only. The antifoam referred to in TABLES 1 and 2 is a polyoxypropylene glycol of nominal molecular weight 1750 which had been "tipped" with ethylene oxide to give a copolymeric product which contained in its molecular structure about 10% by weight of ethylene oxide.

EXAMPLE I

Specimens of various metals were totally immersed for 336 hours in an aqueous solution of an antifreeze composition which was maintained at a temperature of $82^{\circ}\text{C} \pm 1^{\circ}$ and aerated at a rate of 100 ± 10 millilitres per minute. The metal specimens used were those described in ASTM Test Method No. D 1384-61T. The aqueous solution of the antifreeze composition was prepared by mixing 1 part by volume of the antifreeze composition with 2 parts by volume of water containing 100 parts per million of chloride ion (as sodium chloride) and 300 parts per million of sulphate ion (as sodium sulphate). The corrosive properties of the solution containing the antifreeze were evaluated by the weight loss incurred by specimens during the test (calculated in milligrams per square inch) and where an actual gain occurred this is indicated in the results quoted by the addition of the letter "G" after the figures. Each test was run in triplicate. Results obtained with six antifreeze compositions (A to F) which have hitherto proposed, though not necessarily marketed, are

5 given in Table 1. It will be seen that the solu-
tion of the antifreeze composition A is highly
corrosive towards solder and copper, while the
solution of the antifreeze composition B is
highly corrosive to cast iron, steel, aluminium,
solder and copper. Composition C is corrosive
towards cast iron, aluminium and solder. The
compositions D and E are acceptable in this
weight loss test. Weight losses for composition
10 F were likewise acceptable. However, this
composition fails on another important aspect.

For, during the tests fluffy, voluminous white
deposits of hydrated alumina were formed on
the aluminium specimen. This particular form
of aluminium corrosion makes the composition 15
unsuitable for practical purposes, as during its
prolonged use in combustion engines with
aluminium parts, the deposits may be entrained
by the circulating cooling fluid and cause
severe contamination and blocking-up of the 20
narrow passages through the heat exchanger
(radiator).

TSBLE 1

Composition	% by weight	Weight Loss					
		Cast Iron	Steel	Aluminium	Solder	Brass	Copper
A	Sodium benzoate	0.0	0.8	0.1	3.4	0.7	4.9
	Sodium nitrite	0.3	1.1	0.2	6.2	0.6	5.7
	Monoethylene glycol	0.1G	0.0	0.6	7.3	0.6	1.4
B	Sodium tetraborate decahydrate	404	156	10.6	1.5	0.7	4.6
		142	129	9.5	1.5	1.9	14.9
	Monoethylene glycol	91	163	8.5	4.1	1.3	14.7
C	Benzotriazole	97.9	1.1	6.4	8.7	0.4	0.1
	Sodium arsenite	84.7	0.2	10.4	11.6	0.8	0.3
	Disodium hydrogen phosphate						
	Monoethylene glycol	80.8	0.2	17.9	18.4	0.8	0.4
D	Sodium tetraborate decahydrate						
	Sodium metaborate	0.5					
	Dipotassium hydrogen phosphate	1.0					
	Sodium mercaptobenzothiazole	1.5					
	Benzotriazole	0.2	0.44	0.36	0.14	0.51	0.37
	Antifoam	0.05	0.03	1.30	0.37	0.67	0.37
	Monoethylene glycol	0.02	0.44	2.54	0.18	0.65	0.37
E		99.7					
	Dipotassium hydrogen phosphate						
	Sodium mercaptobenzothiazole	2.5	0.13	0.57	0.55	1.02	0.14
	Benzotriazole	0.2	0.0	0.76	0.55	0.81	0.28
	Antifoam	0.05	0.53	0.55	0.83	0.69	0.25
F	Monoethylene glycol	0.02					
		97.3					
	Sodium tetraborate decahydrate						
	Triethanolamine	1.5					
	Phosphoric acid	3.6					
	Sodium nitrite	0.8	1.02	0.74	0.18	0.46	0.62
	Sodium mercaptobenzothiazole	0.25	0.72	0.99	0.23	0.18	0.62
	Antifoam	0.15	0.65	0.86	0.48	0.18	0.67
	Monoethylene glycol	0.02					
		93.7					

EXAMPLE II

Antifreeze compositions 1 to 3 were tested as described in Example I. The results are given in Table 2 from which it can be seen that the anti-corrosion performance in the

weight loss tests is entirely satisfactory. Neither of compositions 1 to 3 formed the fluffy deposits described in the test result of comparative composition F.

TABLE 2

Composition	% by weight	Weight Loss milligrams per square inch					
		Cast Iron	Steel	Aluminium	Solder	Brass	Copper
1	Sodium tetraborate decahydrate	0.5	1.0	0.0	0.3G	0.9	1.1
	Triethanolamine	1.0	0.6	0.0	0.2G	0.1	1.1
	Phosphoric acid	0.4	0.8	0.1G	0.2G	0.0	1.1
	Sodium nitrate						
	Sodium mercaptobenzothiazole						
2	Antifoam						
	Monoethylene glycol						
	Sodium tetraborate decahydrate	1.0G	0.0	0.5	0.6	0.8	0.5
	Triethanolamine	0.5	0.4	0.1	1.0	0.6	0.6
	Phosphoric acid	0.4	0.1	0.2	0.1	0.6	0.8
3	Sodium nitrite						
	Sodium nitrate						
	Sodium mercaptobenzothiazole						
	Antifoam						
	Monoethylene glycol						
3	Sodium tetraborate decahydrate	0.6	1.5	0.2	1.1	0.7	1.4
	Triethanolamine	0.5	1.0	0.3	0.3	0.5	0.7
	Phosphoric acid	0.4	0.5	0.3	0.0	0.1G	1.2
	Sodium nitrate						
	Sodium mercaptobenzothiazole						
3	Antifoam						
	Monoethylene glycol						
	Sodium tetraborate decahydrate						
	Triethanolamine						
	Phosphoric acid						
	Sodium nitrate						
	Sodium mercaptobenzothiazole						
	Antifoam						
	Monoethylene glycol						

EXAMPLE III

To test the performance of antifreeze compositions D and E at various diluted concentrations which may be met in actual practice, i.e. at 5, 10, 15 and 20vol% on the total volume of aqueous antifreeze solutions, aluminium and cast iron test specimen as described in Example I were bolted together and immersed in refluxing aqueous antifreeze solutions for 48 hours. Thereafter the total weight losses of the aluminium specimen (in milligrams) were determined. Weight losses of the cast iron specimen were negligible in all cases.

The results of these tests are included in Table 3.

EXAMPLE IV

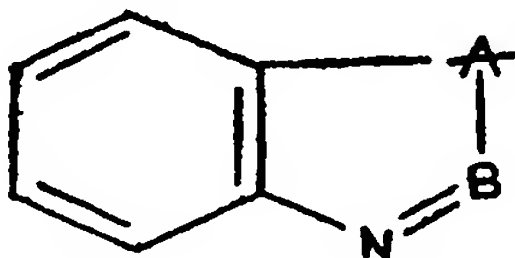
The experiments described in Example III were repeated for compositions 1 to 3. Again, corrosion of cast iron was negligible. The data on aluminum weight losses are included in Table III. From this table it can be seen that the compositions of the invention are by far superior to the comparative compositions D and E, (which were the best ones emerging from the tests of Example I), as regards stability of performance at various concentrations.

TABLE 3

Composition	aluminium weight loss (milligram)			
	5 vol %	10 vol %	15 vol %	20 vol %
D	34.4	39.1	31.0	20.8
E	11.6	13.9	6.6	3.7
1	0.8	1.8	1.4	0.6
2	0.6	0.6	0.6	0.6
3	2.6	2.8	1.8	1.1

WHAT WE CLAIM IS:—

1. An antifreeze composition comprising a water-miscible alcohol, an alkali metal nitrate, and alkali metal metaborate or tetraborate, an alkanolamine phosphate and one or more heterocyclic benzo-compounds with the general formula:



in which the benzene ring optionally contains at least one substituent alkyl radical and B is a CH, CSH or CSM group or a nitrogen atom, M being an alkali metal atom and A representing an oxygen or sulphur atom or a NH group with the proviso that when A is an oxygen or sulphur atom, B represents a CSH or CSM group only.

2. A composition as claimed in claim 1, in which the alcohol is monoethylene glycol.
3. A composition as claimed in claim 1 or 2, in which the alcohol is a mixture of monoethylene glycol and methanol.
4. A composition as in any of claims 1 to 3, in which the phosphate component is di or triethanolamine phosphate.

5. A composition as claimed in any of claims 1 to 4, in which the phosphate component is present in amount of from 0.1 to 5.0% by weight of the antifreeze composition.

6. A composition as claimed in any one of claims 1 to 5, in which the nitrate is a sodium or potassium salt, present in an amount between 0.1 and 1.0% by weight of the antifreeze composition.

7. A composition as claimed in any one of claims 1 to 6, in which the metaborate or tetraborate is a sodium or potassium salt, present in an amount of from 0.1 to 4% weight of the antifreeze composition.

8. A composition as claimed in any one of claims 1 to 7, which additionally contains an alkali metal nitrite.

9. A composition as claimed in claim 8 in which the nitrite is a sodium or potassium nitrite, present in an amount of from 0.1 to 1.5% by weight of the antifreeze composition.

10. A composition as claimed in any one of claims 1—7, in which the heterocyclic compound is sodium mercaptobenzothiazole or benzotriazole.

11. A composition as claimed in any one of claims 1—8, in which the heterocyclic compound is present in amounts between 0.05 and 0.5% by weight of the antifreeze composition.

12. A composition as claimed in claim 1 and substantially as hereinbefore described with particular reference to Examples II and IV.
14. A process as claimed in claim 13, in which the phosphate component is formed in situ. 10
- 5 13. A process for preparing compositions as claimed in any one of claims 1—12, which comprises the addition of the various components to the water-miscible alcohol.

ROY C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1.
Agent for the Applicants.

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